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Effect of fulvic acid surface coatings on plutonium sorption and desorption kinetics on goethite

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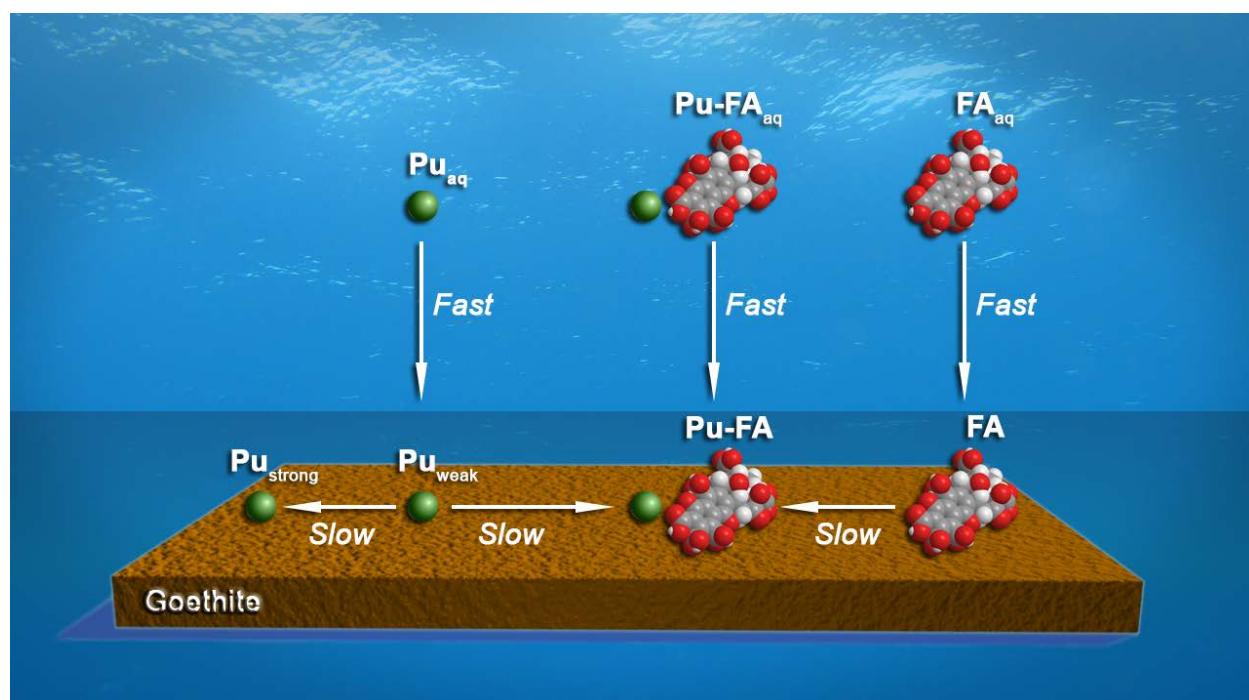
Plutonium, fulvic acid, natural organic matter, sorption, desorption, surface coating, kinetics

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Abstract Art

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29 **ABSTRACT**

30 The rates and extent of plutonium (Pu) sorption and desorption onto mineral surfaces are
31 important parameters for predicting Pu mobility in subsurface environments. The presence of
32 natural organic matter, such as fulvic acid (FA), may influence these parameters. We
33 investigated the effects of FA on Pu(IV) sorption/desorption onto goethite in two scenarios:
34 when FA was (1) initially present in solution or (2) found as organic coatings on the mineral
35 surface. A low pH was used to maximize FA coatings on goethite. Experiments were combined
36 with kinetic modeling and speciation calculations to interpret variations in Pu sorption rates in
37 the presence of FA. Our results indicate that FA can change the rate and extent of Pu sorption
38 onto goethite at pH 4. Differences in the kinetics of Pu sorption were observed as a function of
39 the concentration and initial form of FA. The fraction of desorbed Pu decreased in the presence
40 of FA, indicating that organic matter can stabilize sorbed Pu on goethite. These results suggest
41 that ternary Pu-FA-mineral complexes could enhance colloid-facilitated Pu transport. However,
42 more representative natural conditions need to be investigated to quantify the relevance of these
43 findings.

44

INTRODUCTION

The civil and military use of nuclear power have resulted in an estimated, current worldwide inventory of over 2000 metric tons of plutonium (Pu)¹. Due to its long half-life (24,100 years for ²³⁹Pu) and radiotoxicity (15 pCi L⁻¹ Maximum Contaminant Level in drinking water)², Pu is an important driver in public health risk assessments for nuclear waste repositories. However, an evaluation of risks and the development of reliable, predictive Pu transport models is a challenge. This is in part due to the complex Pu solution chemistry in terms of (1) Pu oxidation states³, (2) low Pu(IV) solubility and the potential formation of intrinsic Pu colloids and nanoclusters^{4, 5}, as well as (3) Pu complexation with various organic and inorganic ligands in solution (e.g., humic and fulvic acids, carbonates, sulfates, phosphates)⁶⁻¹³. In addition, different Pu oxidation states, such as Pu(IV) and Pu(V), show both varying mineral sorption affinities and differences in kinetic sorption rates¹⁴⁻¹⁸ (by definition, the term ‘sorption’ includes all possible processes leading to Pu uptake by the mineral).

The mobility of Pu depends on its chemical speciation, and the biogeochemical conditions found at the source location and along subsequent transport pathways.¹⁹⁻²³ Plutonium mobility in the subsurface is expected to be driven by the advective transport of dissolved Pu species in pore water solutions^{21, 24, 25} or, even more likely, after the association of Pu with mobile mineral or organic-rich colloids²⁶⁻²⁸. In general, the relevance of colloid-facilitated Pu transport is largely determined by ‘stable’ contaminant-colloid binding. Kinetic rates of Pu sorption have to be sufficiently fast and desorption processes slow in order to retain the Pu-colloid association along transport pathways.

Natural organic matter (NOM), such as humic and fulvic acids, is known to affect Pu solution speciation²⁹, sorption behavior^{10, 30, 31}, and mobility³², and may act as an important source³³ or

sink³⁴ for mobile Pu in the environment. With respect to *dissolved NOM*, two primary mechanisms are expected to influence Pu sorption behavior. First, the formation of Pu-NOM solution complexes may directly alter Pu sorption behavior to mineral surfaces.³¹ Second, NOM in solution may control Pu redox chemistry³⁵ and therefore indirectly affect Pu sorption behavior (e.g., the relative abundance of Pu(IV) versus Pu(V) in solution will influence Pu sorption affinities). In addition to dissolved NOM, *organic-rich colloids* can alter Pu partitioning between dissolved, colloidal, and particulate phases and enhance Pu mobility, as has been demonstrated under both laboratory³³ and field conditions^{28, 36}.

Besides dissolved and colloidal organic matter, we believe that the specific role of organic matter coatings, commonly found on mineral surfaces in the environment^{37, 38}, needs to be taken into account for the evaluation of organic matter effects on Pu mobility. Sorbed NOM is known to change mineral surface characteristics^{33, 39, 40}, which may influence Pu sorption and transport behavior. For instance, if NOM increases Pu sorption onto mobile mineral colloids, this could enhance colloid-facilitated Pu transport. In contrast, if the mineral phase is stationary, i.e. as host rock or soil constituents, an increase in Pu sorption will decrease Pu mobility. Further, if NOM limits Pu desorption from the mineral, then we would expect an increase in colloid-facilitated Pu transport, but a decrease in Pu mobility with respect to stationary minerals. Last, organic ligands may strongly affect the underlying pathways of Pu sorption processes, and hence Pu kinetics and the resulting Pu speciation on mineral surfaces. This may further influence the extent and kinetics of later Pu desorption reactions.²⁸

Results from previous studies focusing on the role of organic-rich colloids may not be directly transferrable to questions regarding organic matter coatings, since for environmental colloid samples it is often unknown what fraction of organic ligands is found on colloidal surfaces³³ and

available for reactions with Pu. At this point, investigations of ternary Pu-NOM-solid systems with single, pure mineral phases have included minerals such as silica¹⁸, kaolinite³¹ or gibbsite⁴¹. According to our knowledge, no attempts have been made to investigate Fe-minerals, despite their environmental relevance and the strong sorption affinities of Pu and NOM for these solids.

Hence, the goal of this study was to assess if NOM, initially present in solution or as mineral surface coatings, could alter Pu sorption and desorption kinetics, and stabilize Pu on goethite surfaces (throughout, the term ‘stabilization of Pu’ refers to a stable metal-mineral association). We combined a lab-scale kinetic study with a model-based data interpretation, which included the simulation of Pu and fulvic acid (FA) sorption kinetics, and Pu solution speciation in terms of Pu-FA complexation. This allowed us to determine differences (and similarities) in sorption rates between the various systems, and to develop a conceptual understanding of NOM effects on Pu sorption reactions.

MATERIALS AND METHODS

The mineral (goethite), NOM fraction (fulvic acid) and pH conditions (pH=4) were specifically selected to promote organic ligand sorption onto an environmentally-relevant, pure mineral and to create stable organic coatings on the mineral surface. Further, the conditions of an acidic pH in the presence of Fe-based mineral phases may potentially become relevant in nuclear waste repositories due to the expected corrosion of metal-based waste containers.⁴² Using a radiolabeled form of FA allowed us to cover a wide range of organic ligand concentrations found in nature (0.5-50 mg L⁻¹ TOC).

Materials

All solutions were prepared using ultrapure Milli-Q water and reagent grade chemicals. Solutions, glassware and other equipment were autoclaved whenever feasible. Goethite (α -FeOOH) was made by precipitation of 1 M Fe(NO₃)₃ in 5 M KOH following the recommendations of Schwertmann and Cornell.⁴³ X-ray diffraction (XRD) of the dried solids (Bruker D8 X-ray diffractometer) confirmed goethite as the major phase (mineral powder diffraction file 01-074-2195). BET analysis (Quadrasorb SI surface area analyzer with QuadraWinTM v.5.02 software, Quantachrome Instruments) determined a specific surface area of $20.6 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$; potentiometric titrations a point-of-zero charge of 6.9. Furthermore, SEM micrographs taken of a previously-prepared goethite, following the same procedure, showed 1 to 3 μm long acicular crystals (needles), larger aggregates, and some star shaped particles⁴⁴. Prior to experiments, goethite stock suspensions (approximately 20 or 25 g L⁻¹ solid) were prepared in a background electrolyte with the same chemical composition as in later experiments (pH=4, 0.01 M NaCl), and centrifuged and decanted three times to remove fines (<183 nm). Exact solid concentrations (14.015 and 19.362 g) were then determined by weight, after drying out triplicate suspension samples (5 or 2 mL) at 40 °C.

In all experiments, Pu was added as Pu-238 and analyzed by liquid scintillation counting (LSC) (Perkin Elmer Tri-Carb 2900TR Liquid Scintillation Analyzer, Ultima Gold liquid scintillation cocktail). Prior to experiments, Pu-238 stock solutions (in-house, or purchased from Isotope Products Laboratories) were purified using 1 mL beds of BioRad AG[®]1×8, 100–200 mesh anion exchange resin in BioRad Poly-Prep chromatography columns (loading in 8 M HNO₃, elution in 1 M HCl). Solvent extraction⁴⁵ was used to confirm a predominant Pu(IV) oxidation state in Pu-238 stock solutions (> 90% Pu(IV)), and to characterize potential changes in Pu oxidation state in binary Pu-goethite kinetic experiments (a detailed characterization of Pu

oxidation states in the presence of FA was not feasible due to the known interferences of organic ligands in Pu solvent extractions).

A standardized form of FA (Suwannee River FA, Standard I, 1S101F, International Humic Substances Society) was selected. For analytical reasons, a tritium-labeled FA tracer was used, which shows the same sorption behavior onto Fe-oxides as unlabeled FA, as well as long-term chemical stability and an even distribution of the ^3H -label over the entire FA molecular size range.⁴⁶ The Pu-238 counting window was adjusted to 50-500 keV in order to exclude any potential contributions of tritium counts (0-18.6 keV; $E_{\text{Tritium}}=0.47$) and to isolate potential FA luminescence effects (18.6-50 keV) at high FA concentrations. Nevertheless, a few supernatant samples were selected to confirm the direct correlation between measured Total Organic Carbon (TOC) concentrations (Sievers 5310C) and TOC concentrations calculated based on tritium counts (29 samples; $R^2=0.99$; for details, see Supporting Information (SI), Figure S1).

Overview of kinetic sorption/desorption experiments

We performed two types of kinetic sorption/desorption experiments, which differed in the way Pu was introduced into the systems. In *pre-complexation* experiments, Pu was allowed to complex with solution-phase FA prior to metal sorption to goethite. In *pre-coating* experiments, the goethite surface was coated with FA before soluble Pu was added to the system. Pu sorption in these experiments was compared to metal sorption in a FA-free, binary Pu-goethite system. Plutonium-goethite sorption/desorption experiments (in triplicates) followed the same, general procedure as *pre-complexation* experiments, except that ligand-free Pu solutions were prepared shortly prior to the start of kinetic experiments to minimize Pu sorption onto container walls. For all experimental setups, a desorption step was performed after the initial Pu sorption by replacing

the background electrolyte with fresh, FA-free, Pu-free electrolyte. This allowed us to evaluate potential differences in Pu desorption behavior between FA-containing and FA-free systems.

The chemical composition of the background electrolyte was held constant (pH=4, I=0.01 M NaCl) during all experiments. Solution pH was adjusted, as needed, with small volumes of dilute HCl and NaOH. Concentrations of goethite (2 g L^{-1}), total Pu ($10^{-10} \text{ M Pu}_{\text{Tot}}$, 14.8 kBq L^{-1} =400 nCi L^{-1} Pu-238) and tritium-labeled FA (40.7 kBq L^{-1} =1.1 microCi L^{-1}) were the same in all sorption experiments. The selection of the total Pu concentration was driven by analytical detection limits, the convenient use of liquid scintillation counting for a large number of samples, and a straight-forward separation of Pu (alpha) and tritium (beta) counts during counting while aiming for the lowest, most environmentally-relevant Pu concentration possible. However, total FA concentrations were varied over three orders of magnitude (0.5, 5 and 50 mg L^{-1} TOC; equivalent to 0.95, 9.54, 95.35 mg L^{-1} FA)⁴⁷ by adding increasing amounts of unlabeled FA (negligible TOC contributions of tracer with $\sim 1 \mu\text{g L}^{-1}$ TOC.)

In order to characterize the nature of sorbed FA, parallel sorption experiments were performed with larger sample volumes ($V_{\text{Tot}}=900 \text{ mL}$) and at the highest FA concentration only, due to analytical limitations (for details, see SI). Supernatant fractions at various time points were compared with unreacted FA based on results from ^1H nuclear magnetic resonance (NMR) spectroscopy and a size-characterization method coupling Field-Flow-Fractionation (FFF) with UV absorbance and ICP-MS Fe analysis. Our goals were: (1) to investigate potential changes in FA surface characteristics over a FA sorption equilibration of five days, which could be relevant for Pu sorption kinetics/behavior in *pre-complexation* experiments over the same time-frame, and (2) to gain a basic understanding of the characteristics of FA surface coatings after a 5-day sorption equilibration, the initial conditions for Pu sorption in *pre-coating* experiments.

Pu-FA *pre-complexation* sorption/desorption experiments

For Pu-FA *pre-complexation* sorption/desorption experiments, solutions comprising autoclaved Milli-Q water, 1 M NaCl, regular and tritium-labeled FA, and Pu-238 were added to autoclaved 175 mL polycarbonate (PC) centrifuge vials to achieve the desired solute concentrations in the final suspension volume ($V_{\text{Tot}}=160$ mL). After pH adjustment (pH=4), solutions were allowed to equilibrate overnight (≥ 18.3 hours). The sorption step was initiated by pipetting an exact volume of goethite stock suspensions (pH=4) into the PC vials containing Pu-FA solutions, resulting in a total volume of 160 mL. After brief manual shaking, suspension fractions were sampled (1.9 mL), centrifuged to remove goethite particles >100 nm from solution (Beckman Coulter Allegra 21R centrifuge, Beckman F2402H rotor, 10,000 rpm over 7 minutes), and analyzed for Pu-238 and ^3H -FA by LSC (in duplicate). Over the 7-day sorption period, the continuous agitation of samples on a shaking table in the dark was periodically interrupted to sample and analyze goethite suspensions in the same manner. Sampling times were defined as the time-points when sample centrifugation was started and solute-mineral interactions were interrupted. Finally, the sorption step was completed by centrifuging the remaining sample suspensions (105.8 mL, accounting for all types of supernatant analysis) in the 175-mL PC vials. pH measurements of the suspensions confirmed that only minimal pH drifts occurred over sorption periods (average initial sample pH=4.01; pH-shifts ≤ 0.09). Supernatant solutions were sampled directly from the PC vials for the last sorption time-point. Then, the majority of the supernatant was removed by pipetting, and the remaining supernatant volume determined by weight difference.

For the desorption step, fresh background electrolyte was added to maintain a calculated solid concentration of 2 g L^{-1} goethite. The solids were re-suspended through shaking and sonication over 3 minutes. This initiated the 14-day desorption step, which involved repeated suspension sampling and supernatant analysis as described above. For the data interpretation of desorption results, measured supernatant concentrations were mathematically corrected for the contributions of Pu counts from the small volume fractions remaining in the systems after the initial sorption steps ($\leq 7.6\%$ of experimental volumes during desorption steps).

Pu-FA *pre-coating* sorption/desorption experiments

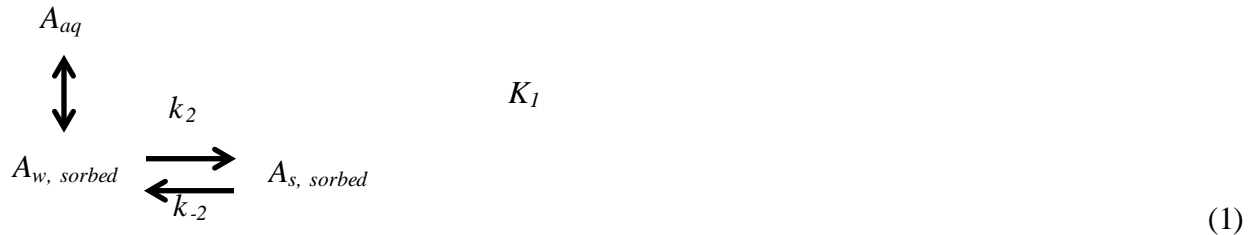
In *pre-coating* experiments, FA solutions of 0.5, 5 and 50 mg L^{-1} TOC were prepared in background electrolyte at pH=4 and allowed to equilibrate over approximately two hours. Goethite stock suspensions (pH=4) were then added to give 2 g L^{-1} solid in total volumes of 179 mL (increased sample volumes accounted for volume fractions to be removed during coating). To characterize FA sorption to goethite, suspension fractions were sampled, centrifuged, and analyzed for FA solution concentrations by LSC. Samples were allowed to equilibrate over 5 days until apparent steady-state conditions were achieved.

The coating step was terminated by separating the solid from solution through centrifugation (100 nm size cut-off). Supernatant solutions were sampled for FA analysis, and the majority of the remaining volume was removed by pipetting. Then, pH-adjusted Pu-238 was added to each PC vial to create a 10^{-10} M Pu(IV), 2 g L^{-1} goethite suspension in 160 mL. After re-suspending the solid by shaking, the same experimental Pu sorption and desorption steps were followed as described for *pre-complexation* experiments above.

For all sorption experiments, goethite-free controls were set up to characterize Pu losses due to metal sorption onto “bare” (*pre-complexation* experiments) or “FA-coated” (*pre-coating* experiments) container walls (details and Figure S6, SI). In these controls, the observed Pu wall sorption represents a ‘worst-case-scenario’ due to the absence of competing goethite surfaces, which, most likely, would lead to an overestimation of Pu wall sorption effects if wall sorption data were directly transferred from goethite-free to goethite-containing systems. For instance, in goethite-containing samples, solids provide 99.82% of the total surface area; container walls (assuming a uniform surface) only 0.18%.

Kinetic modeling

The modeling of Pu and FA sorption kinetics was based on a simple empirical model, which includes an initial, fast equilibrium sorption reaction followed by an optional, consecutive, kinetically-controlled first-order reversible process (eq 1).



In eq 1, A refers to Pu, FA, or Pu-FA complexes, that are either present in solution (subscript *aq*) or sorbed to the mineral surface (subscript *sorbed*). The subscripts *w* and *s* indicate weak and strong sorption sites respectively. Both weak and strong sorption sites may reflect the formation of binary or ternary surface complexes. The initial sorption reaction is considered an equilibrium reaction with a unitless equilibrium constant defined as

$$K_1 = \frac{[A_{w, sorbed}]}{[A_{aq}]}
 \tag{2}$$

247 The following, consecutive reaction,

$$248 \quad \frac{d[A_{s,sorbed}]}{dt} = k_2[A_{w,sorbed}] - k_{-2}[A_{s,sorbed}], \quad (3)$$

249 represents a kinetically-limited first-order reversible sorption reaction such that

$$250 \quad K_2 = \frac{k_2}{k_{-2}}. \quad (4)$$

251 For simplicity, $[A_{aq}]$, $[A_{w,sorbed}]$, and $[A_{s,sorbed}]$ are in units of mol L^{-1} , while rate constants (k_2 and
 252 k_{-2}) have units of reciprocal hours. All fitting parameters (K_1 , k_2 , k_{-2}) were determined by using
 253 the solver function in Excel 2007 while minimizing the difference between experimental and
 254 simulated Pu and FA solution concentrations (log scale). Simulated solution concentrations at
 255 time t were based on the difference between initial solution concentrations at time zero and
 256 sorbed concentrations at time t , namely

$$257 \quad [A_{w,sorbed}]_t = K_1[A_{aq}]_t \quad (5)$$

$$258 \quad \text{and} \quad [A_{s,sorbed}]_t = [A_{s,sorbed}]_{t-1} + k_2[A_{w,sorbed}]_{t-1}\Delta t - k_{-2}[A_{s,sorbed}]_{t-1}\Delta t. \quad (6)$$

259 The sorption distribution coefficients (K_d values in mL g^{-1}) for the first reaction step (K_{d1}) and
 260 the overall reaction including both reaction steps (K_{dT}) at $t \rightarrow \infty$ are calculated as

$$261 \quad K_{d1} = K_1 \times \frac{V}{m} \quad (7)$$

262 and

$$263 \quad K_{dT} = (K_1 + K_1 K_2) \frac{V}{m} \quad (8)$$

264 where V and m refer to solution volume (mL) and solid mass (g), respectively.

265 Overall, this concept is equivalent to the consecutive multi-reaction model described in
 266 Tinnacher *et al.* (2011) for Np(V) sorption/desorption to goethite.⁴⁴ It is important to note that
 267 this conceptual model is not intended to reflect any specific mechanistic processes but to provide

an objective, mathematical tool to identify relevant differences (or similarities) in the kinetic sorption behavior of Pu, FA and Pu-FA solution complexes.

Chemical speciation modeling

Chemical speciation modeling was limited to predicting the relative abundance of free and FA-complexed Pu in the aqueous phase at pH=4. The relative abundances were calculated using experimental partitioning data and an empirical model based on mass action considerations (for details, see SI and Figures S7, S8). Data fitting resulted in the following equation

$$\frac{f_{\text{PuFA}}}{(1-f_{\text{PuFA}})} = 0.10[\text{FA}]^{0.68} \quad (9)$$

where f_{PuFA} is the unitless fraction of complexed Pu and [FA] is the FA solution concentration in mg L⁻¹ TOC. Equation 9 is only valid for a solution at pH=4 with a total Pu concentration of 10⁻¹⁰ M. Based on equation 8, the concentrations of Pu-FA complexes in equilibrium with 0.5, 5, and 50 mg L⁻¹ TOC are 6.2×10^{-12} , 2.4×10^{-11} , and 6.0×10^{-11} M, respectively, representing 6%, 24% and 60% of total Pu being complexed.

RESULTS AND DISCUSSION

Pu sorption to goethite

In the following, kinetic data are presented on logarithmic time-scales to highlight kinetic differences between systems at early time-frames in the experiments. The same kinetic data are also shown using linear time-scales in SI. A good reproducibility of Pu sorption data was demonstrated based on the results from binary Pu-goethite sorption experiments performed in triplicates (Figure S9, SI).

In the absence of FA, Pu sorption onto goethite is characterized by a very rapid initial uptake (removal of 48% of solution-phase Pu after ten minutes), followed by a period of slower sorption over 24 hours (Figure S9, SI; average values in Figure 1). After this, the Pu solution concentration does not change appreciably over the remainder of the 7-day sorption experiment. The resulting Pu surface loading ($3.9 \times 10^{-11} \text{ mol g}^{-1}$ or $1.9 \times 10^{-12} \text{ mol m}^{-2}$) is in excellent agreement with comparable literature data ($1.8 \times 10^{-12} \text{ mol m}^{-2}$ at pH=4 after 24-hour equilibration)¹⁶. A limitation in goethite surface sites for Pu sorption reactions is not expected at this total Pu concentration (10^{-10} M), given that the total surface site concentration was estimated at $1.6 \times 10^{-4} \text{ M}$ based on the specific surface area ($20.6 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$) for goethite and an assumed surface site density of $2.31 \text{ sites nm}^{-2}$ ⁴⁸.

Plutonium oxidation state analysis indicated >90% Pu(IV) in the stock solution. However, a rapid transformation of Pu(IV) into Pu(V) at the beginning of the sorption experiment cannot be ruled out. After 7-day sorption equilibration, the remaining Pu in solution was predominantly Pu(V) (82%), with lower contributions from the non-extractable fraction (8%), Pu(VI) (5.1%) and Pu(IV) (4.8%). A similar change in the dominant aqueous Pu oxidation state from Pu(IV) to Pu(V) during sorption equilibration has been observed for kaolinite systems at pH=4.³⁵ Previous work has indicated a very low sorption affinity for Pu(V) on goethite at pH<5.^{16, 17}

In the absence of FA, an adequate model fit to Pu sorption data required both an equilibrium and a kinetically-controlled sorption reaction (Table 1; Figure S9, SI). The slow, kinetically-controlled reaction has an average forward reaction rate of 0.16 hr^{-1} and leads to a 7-day equilibrium K_{dT} of $2,100 \pm 200 \text{ mL g}^{-1}$. Powell et al. (2005) determined an apparent surface-normalized Pu(V) sorption rate constant on goethite of $0.003 \text{ L m}^{-2} \text{ hr}^{-1}$ at pH=5.7, and attributed slow sorption of Pu to a surface-mediated reduction of Pu(V) to Pu(IV).¹⁷ A comparable value

computed from our data ($0.004 \text{ L m}^{-2} \text{ hr}^{-1}$), in conjunction with the observed predominance of Pu(V) in supernatant solutions, suggests that Pu(IV)/Pu(V) redox processes on the goethite surface may be controlling Pu sorption rates in our systems.

Fulvic acid sorption onto goethite

Identical experimental setups for *pre-complexation* and *pre-coating* experiments allowed for a comparison of FA sorption kinetics in the presence and absence of 10^{-10} M Pu over 5 days. Overall, Pu-FA solution complexation does not have any apparent effect on FA sorption kinetics (Figure 2), which is perhaps to be expected given the low concentration of Pu (10^{-10} M) compared to FA functional groups ($\sim 10^{-6}$ - 10^{-4} M , details below). In both systems, FA sorption is very fast, reaching apparent steady-state conditions within four hours or less.

Due to fast FA sorption and the lack of an observable slow sorption period, FA sorption kinetics could be simulated with a simple equilibrium term, and without the need for a consecutive reaction (Figure 2). At total FA concentrations of 0.5 and 5 mg L^{-1} TOC, simulated FA sorption distribution coefficients (K_{dT}) are similar in *pre-complexation* (2,100 and 1,900 mL g^{-1} , respectively) and *pre-coating* (2,000 and 1,800 mL g^{-1} , respectively) experiments after five days. However, at 50 mg L^{-1} TOC, K_{dT} values are lower in both cases (550 and 420 mL g^{-1} , respectively). This suggests a mineral surface site limitation based on mass action considerations. We estimated a total, reactive site concentration of $1.6 \times 10^{-4} \text{ M}$ for goethite, given the measured surface area of $20.6 \text{ m}^2 \text{ g}^{-1}$ and assuming a site density of $2.31 \text{ sites nm}^{-2}$ ⁴⁸. In contrast, at 50 mg L^{-1} TOC, the FA ligand concentration is estimated to be at an approximately 4-time excess ($6.1 \times 10^{-4} \text{ M}$) relative to surface sites, assuming a primary involvement of carboxylic acid groups at pH=4 ($6.45 \text{ mmol}_{\text{carboxylic groups}}/\text{g}_{\text{FA}}$; 53% TOC-content

for FA⁴⁷). In comparison, at 0.5 and 5 mg L⁻¹ TOC, we estimate FA functional group concentrations of 6.1×10^{-6} M and 6.1×10^{-5} M, respectively.

A comparison of NMR spectra collected for unreacted (goethite-free) and residual FA after sorption suggests a preferential sorption of larger, more aromatic compounds (6-8 ppm) at short sorption times (Figure 3; for details, see SI). Experimentally, this conclusion is based on FA supernatant fractions that appear less aromatic than the source FA. The aromatic fraction was identified as large molecules by Haiber et al. (2001).⁴⁹ Over time (after 3 and 5 days) we observe a reduction in the intensity of the aliphatic molecule peaks (1-3 ppm)⁴⁹ relative to the aromatic molecule peaks in the supernatant. This indicates that these fractions, previously identified as smaller molecules⁴⁹, may begin to sorb to the surface after longer time-frames. A specific quantification of the ¹H signals in these fulvic acid samples are hindered by broad overlapping peaks, the presence of the triplet from ammonium in the aromatic region (6 – 8 ppm), and by distorted line shapes in the center of the spectra due to incomplete or imperfect suppression of the water peak (for details, see SI).

Results from FA size characterizations by FFF-UV absorbance (Figure S4, SI) further support a slight decrease in the average molecular size between unreacted and residual FA after sorption, as indicated in UV-fractograms by a decrease in tailing and a slight shift in the maximum peak position to shorter retention times. However, no significant changes in the residual FA size distribution in supernatant solutions were observed within FFF detection limits over time (4-hour versus 5-day sample). Based on these results, we conclude that only minor changes occur in the fractionation between solution- and solid-phase FA during the sorption time-frame in *pre-complexation* experiments after initial FA sorption, leading to minimal or no effects on Pu sorption kinetics. Furthermore, organic-mineral coatings, prepared in *pre-coating* experiments

prior to Pu contact with the mineral, predominantly consist of large, aromatic compounds with minor contributions of small, aliphatic structures.

Pu sorption in *pre-complexation* experiments

In *pre-complexation* experiments, Pu was equilibrated with FA prior to sorption onto goethite. After 7-day sorption equilibration, the presence of FA increases the fraction of Pu sorbed from $81 \pm 2\%$ in binary systems to 92-97 % over the range of tested FA concentrations (Figure 1). Modeling results, in terms of 7-day K_{dT} values, support this conclusion with simulated K_{dT} values of 2,100 and 7,000 mL g⁻¹ in the absence and presence of 0.5 mg/L TOC, respectively. In addition, at 5 and 50 mg L⁻¹ TOC concentrations, the presence of FA dramatically increases long-term equilibrium K_{dT} values. These results demonstrate that the presence of FA enhances Pu affinity for goethite at pH=4.

It is important to note that any enhancement in metal sorption in the presence of organic matter is expected to be highly dependent on pH⁵⁰, mineral and organic matter characteristics, and the specific pH-dependence of organic matter sorption for a given mineral. For instance, Roberts et al., (2008)¹⁸ found that, at pH=8.2, Pu sorption to silica was decreased if Pu(IV) was pre-equilibrated with humic acid prior to any metal-mineral contact. Blinova et al., 2007⁵¹ argued that Pu-FA complexation will result in more mobile Pu(IV) species at higher pH values (i.e., pH=6), where one would expect lower FA sorption and larger FA fractions remaining in solution. Last, Xu et al., 2014³³ determined that, at increasing pH values, larger fractions of Pu became associated with organic-rich colloids compared to the particulate phase of an environmental soil sample.

The weaker sorption of Pu at 50 mg L⁻¹ TOC (simulated K_{dT} 7,600 mL g⁻¹) compared to 5 mg L⁻¹ TOC (simulated K_{dT} 17,000 mL g⁻¹) is consistent with the mineral surface site saturation observed for binary FA-goethite systems at this concentration. Surface saturation with FA, coupled with the availability of appreciable FA concentrations remaining in solution, may result in a small competition between surface- and solution-phase FA for Pu at this concentration. Interestingly, Pu interactions with polycarbonate container walls in mineral-free controls follow similar trends (Figure S6, SI); the presence of FA reduces Pu wall sorption, possibly due to the formation of Pu-FA complexes in solution.

In terms of FA effects on Pu sorption kinetics, the presence of organic ligands accelerates overall Pu sorption rates compared to FA-free systems in *pre-complexation* experiments. Pu sorption reaches equilibrium conditions almost immediately at the two higher FA concentrations. However, at 0.5 mg L⁻¹ TOC, a kinetic component for Pu sorption reactions is observed. At this FA concentration, Pu-FA solution speciation calculations indicate that only 6% of Pu (6.2×10^{-12} M) is complexed with FA. This low fraction of complexed Pu may be the result of our specific experimental conditions and metal-ligand concentration ratio of 1.6×10^{-5} (with 10^{-10} M total Pu and 6.1×10^{-6} M FA carboxylic groups). Nevertheless, the low degree of Pu-FA solution complexation suggests that Pu sorption behavior should be similar to binary Pu-goethite systems (assuming a comparable distribution of Pu oxidation states in solution). Indeed, the simulation of Pu sorption kinetics in the presence of 0.5 mg L⁻¹ TOC required both, an initial sorption (K_{dl}) and a kinetically-controlled reaction, consistent with binary Pu-goethite systems. However, the initial sorption step is characterized by a substantially higher K_{dl} (2,800 mL g⁻¹) compared to the binary system (470 mL g⁻¹; Table 1).

Thus, it appears that FA has a strong effect on Pu sorption even at a relatively low FA concentration, where Pu-FA complexation is not expected to dominate aqueous Pu speciation. Given that in Pu-goethite systems the reduction of solution phase Pu(V) to Pu(IV) is likely to control Pu sorption kinetics, we assume that FA serves to stabilize a fraction of Pu(IV) in solution at this low concentration. This is consistent with previous studies that have found a rapid reduction of Pu(V) to Pu(IV) in the presence of humic substances^{51, 52}. Furthermore, results from Pu-FA complexation experiments (see SI for details) indicate the presence of large fractions of Pu(IV) in equilibrium with Pu-FA solution complexes at higher, total FA concentrations (e.g., ~76% at 5 mg L⁻¹ TOC). At this point, the specific mechanisms behind this potential FA control of the oxidation state of uncomplexed Pu in solution are unknown and require further investigation. However, possible explanations include (1) a sequestration of oxygen by FA leading to a reduction of the redox potential, which further prevents the formation of Pu(V) or (2) a reduction of Pu(V) to Pu(IV) by FA, followed by the dissociation of the resulting Pu(IV)-FA complexes.

At FA concentrations of 5 and 50 mg L⁻¹ TOC, Pu sorption is dominated by fast equilibrium sorption with a small, if any, observable kinetic component (Figure 1; Table 1). This suggests that Pu sorption is controlled by the kinetic sorption behavior of Pu-FA complexes, rather than a mixture of Pu-FA complexes and Pu(IV/V) ions, as expected at the lowest FA concentration. However, we cannot rule out the possibility that these higher concentrations of FA also promote a more rapid reduction of residual Pu(V) to Pu(IV), as has been previously observed for Pu(V)-organic matter systems^{51, 52}. Overall, changes in Pu sorption kinetics in the presence of FA suggest that FA may alter Pu surface speciation and, in turn, Pu desorption behavior.

Pu sorption in *pre-coating* experiments

In *pre-coating* experiments, FA was sorbed to goethite prior to Pu addition (Figure 2). This resulted in different FA surface concentrations at the beginning of the Pu sorption step (0.19, 1.88, 10.97 mg TOC g_{goethite}⁻¹) depending on the initial FA concentrations during coating (0.5, 5, 50 mg L⁻¹ TOC). Fulvic acid desorption during the Pu sorption step was very slow/minimal, leading to maximum aqueous FA concentrations of 0.01, 0.11 and 1.14 mg L⁻¹ TOC in the order of increasing initial FA concentrations. While this suggests reasonably-stable organic-mineral surface coatings, and low concentrations of solution- compared to solid-phase FA, aqueous FA in *pre-coating* experiments may still have some effect on Pu solution speciation, particularly at the highest FA concentration.

Based on experimental data, Pu sorption behavior in *pre-coating* experiments is different from that in both, binary Pu-goethite and *pre-complexation* experiments (Figure 1). Furthermore, there appears to be a greater dependence of Pu sorption rates on FA concentrations in *pre-coating* compared to *pre-complexation* systems. For instance, in the 0.5 mg L⁻¹ TOC *pre-coating* experiment, initial Pu sorption was similar to that observed in binary Pu-goethite systems, while sorption was higher at 5 mg L⁻¹ TOC. At these concentrations, slow Pu sorption continued over longer time-frames and appeared to slowly approach the same steady-state values as observed in *pre-complexation* experiments. At 50 mg L⁻¹ TOC, initial Pu sorption was much greater than in binary systems and steady-state was reached more rapidly.

Based on modeling results, Pu sorption is kinetically-controlled at *all* tested TOC concentrations in *pre-coating* experiments (data fitting required consecutive, kinetically-controlled surface reactions), while this is the case only at the lowest FA concentration in *pre-complexation* experiments. This kinetic control becomes apparent early on in the experiments,

which is reflected by different K_{dl} values simulated for the two types of experimental setups. However, this decrease in Pu sorption rates, relative to comparable systems in *pre-complexation* experiments, is highly dependent on FA concentrations. This is possibly due to a balance between the kinetic effects of solution-phase FA, accelerating Pu sorption rates, and solid-phase FA, slowing down Pu surface reactions. This effect of solid-phase FA on Pu sorption kinetics may be due to a kinetic transition of Pu surface species from sites associated with the ‘bare’ mineral to sorbed FA, as has been suggested for an organic-rich soil previously³³.

In order to evaluate the influence of solution- versus solid-phase FA in *pre-coating* experiments, we can compare Pu sorption behavior in *pre-complexation* experiments at 0.5 and 5 mg L⁻¹ initial TOC with the *pre-coating* experiment at 50 mg L⁻¹ TOC, which resulted in a similar solution-phase TOC (1.14 mg L⁻¹) but in the presence of a high FA surface concentration (10.97 mg TOC g_{goethite}⁻¹; Figure 1). Based on this comparison, we conclude that, while solution-phase FA may have some influence on accelerating Pu sorption kinetics in the 50 mg L⁻¹ TOC *pre-coating* experiment, it is not the main driver controlling overall rates. Solid-phase FA, and its effects on mineral surface characteristics, primarily determine Pu sorption rates and cause a shift to slower Pu sorption kinetics.

Last, our data also suggest the formation of ternary surface complexes at the highest FA concentration in *pre-coating* experiments. This is due to the fact that, in the absence of a ternary complex, Pu sorption should decrease as the goethite surface becomes saturated with FA. Since a surface site limitation was observed for FA but not for Pu at this concentration, we conclude that it is a Pu-FA ternary complex rather than a Pu-FA solution complex which controls Pu sorption in *pre-coating* experiments.

Pu and FA desorption kinetics

Following the Pu sorption steps in *pre-coating* and *pre-complexation* experiments, supernatant solutions were replaced with fresh, Pu- and FA-free electrolyte to examine Pu and FA desorption behavior from goethite. Concentrations of desorbed FA are rather small (Figure S13, SI), with comparable FA fractions ($\leq 5\%$) being remobilized at all initial FA surface concentrations.

A valid evaluation of Pu desorption behavior needs to take into account the differences in Pu surface concentrations at the beginning of desorption steps in binary and ternary systems. For this purpose, we computed fractions of desorbed Pu (Figure 5) based on each initial Pu surface concentration for exactly the same desorption time-frame (14.0 days). This calculation was based on a linear regression of the last four desorption data points in each dataset using the Microsoft EXCEL “Linest” function, which provides standard deviations for calculated slopes and intercepts. The latter further allowed us to compute propagated errors for fractions of desorbed Pu.

Based on this comparison, smaller fractions of Pu are desorbed from goethite when FA is present (Figure 5). In particular, less Pu is desorbed with increasing FA surface concentrations, once a FA threshold concentration of $\sim 0.20 \text{ mg TOC/g}_{\text{goethite}}^{-1}$ is exceeded, which is the FA surface concentration in *pre-complexation* and *pre-coating* systems at an initial, total FA concentration of $0.5 \text{ mg L}^{-1} \text{ TOC}$ (lowest-concentration data points in Figure 5). Hence, Pu release from goethite is not primarily driven by FA desorption from the mineral. Furthermore, elevated FA surface concentrations ($\geq 1.9 \text{ mg TOC g}_{\text{goethite}}^{-1}$) appear to slow down Pu desorption kinetics within the time-frames evaluated in this study. This finding is in agreement with previous results suggesting that a fraction of Pu(IV) may become ‘irreversibly’ sorbed to silica when Pu is complexed with humic acid prior to metal contact with the mineral phase¹⁸.

This inverse relationship between FA concentration and Pu desorption suggests that, under the given pH conditions, ternary surface complexes are likely more stable than binary Pu-goethite complexes on the goethite surface. This is also in accordance with modeling results, which indicate higher Pu K_{dT} values for Pu sorption in most systems containing FA. Moreover, the ability of FA to stabilize Pu on goethite surfaces appears to be independent of the order of FA addition, as tested in *pre-complexation* and *pre-coating* experiments.

Potential effects of dissolved FA on sorbed Pu

Based on results from *pre-complexation* and *pre-coating* experiments, we can make some hypotheses regarding the behavior of sorbed Pu, after its contact with solutions containing FA. We believe that the stability of surface Pu will largely depend on the relative differences between kinetic rates of FA sorption versus Pu desorption, followed by Pu-FA solution complexation. If FA sorption is very fast, then sorbing FA could potentially ‘coat’ surface Pu, leading to a comparable or higher stabilization of sorbed Pu as observed in previous experiments. In contrast, if FA sorption is relatively slow, then dissolved FA may lead to enhanced Pu desorption during the experimental FA sorption step, based on mass action considerations.

ENVIRONMENTAL IMPLICATIONS AND RECOMMENDATIONS

Fulvic acid (FA) has the potential to influence plutonium (Pu) sorption kinetics in three ways: (1) by controlling Pu oxidation states in solution, e.g. by stabilizing Pu in the +4 oxidation state; (2) by the formation of Pu-FA solution and/or ternary surface complexes; and (3) by the possible slow transformation of binary Pu surface complexes to more stable ternary complexes. Differences in Pu sorption kinetics in the presence and absence of FA are indicative of different,

overall metal sorption mechanisms. These, in turn, can lead to changes in Pu surface speciation and desorption behavior.

In this current work, we investigated the impact of FA on Pu sorption/desorption on goethite at pH=4, while FA was present in solution or in the form of organic coatings on the mineral. In general, the presence of FA increased Pu sorption affinities for goethite at this acidic condition. In addition, FA caused changes in Pu sorption kinetics in all ternary systems tested, with higher Pu sorption rates in the presence of solution-phase FA and lower rates in the presence of organic coatings. Independent of the initial form of FA, FA also stabilized Pu on the mineral surface above a solid concentration of $\sim 0.20 \text{ mg TOC g}_{\text{goethite}}^{-1}$.

We used organic ligand concentrations comparable to those in natural waters,^{30, 53} and took into account the environmental relevance of organic matter coatings^{37, 38}. Thus, our results provide evidence that the presence of FA may contribute to increased sorption of Pu to Fe-oxides in low-pH environments. Under the appropriate conditions, this increase in Pu sorption affinity could serve to enhance the amount of Pu involved in colloid-facilitated transport, or increase Pu retention on a host rock. The suppression of Pu desorption from the mineral in the presence of organic matter would further strengthen these effects. Furthermore, potential changes in Pu sorption/desorption kinetics in the presence of organic ligands need to be considered while evaluating the potential relevance of Pu colloid-facilitated transport. Future investigations should be aimed at expanding these experiments to other pH values and lower, more environmentally-relevant Pu concentrations. Furthermore, it would be useful to evaluate the effects of competing ions on Pu-ligand complexation, to characterize the effects of sorbed organic matter on the surface site concentration and specific surface area of goethite available for Pu sorption reactions, and to test different mineral types.

SUPPORTING INFORMATION

Supplementary data, where noted in the text, is available free of charge via the Internet at <http://pubs.acs.org/>.

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TABLES

Table 1. Summary of model parameters used to fit Pu and fulvic acid sorption data.

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| | K_1 | K_{d1} | k_2 | k_{-2} | K_{dT} |
|--|----------|----------|------------------|--------------------|--------------------|
| | unitless | mL/g | hr ⁻¹ | hr ⁻¹ | mL/g |
| ----- Binary: Pu --> goethite ----- | | | | | |
| Pu sorption | | | | | |
| Replicate 1 | 1.1 | 550 | 0.20 | 0.065 | 2200 |
| Replicate 2 | 0.91 | 460 | 0.15 | 0.051 | 1800 |
| Replicate 3 | 0.81 | 400 | 0.13 | 0.028 | 2200 |
| ----- Pre-complexation: Pu-FA --> goethite ----- | | | | | |
| Pu sorption | | | | | |
| 0.5 ppm C | 5.7 | 2800 | 0.56 | 0.38 | 7000 |
| 5 ppm C | 25 | 12000 | - | - | 17000 ^b |
| 50 ppm C | 11 | 5700 | - | - | 7600 ^b |
| FA sorption | | | | | |
| 0.5 ppm C | 3.8 | 1900 | - | - | 2100 ^b |
| 5 ppm C | 3.6 | 1800 | - | - | 1900 ^b |
| 50 ppm C | 1.0 | 510 | - | - | 550 ^b |
| ----- Pre-coating: Pu --> FA-goethite ----- | | | | | |
| Pu sorption | | | | | |
| 0.5 ppm C | 0.91 | 460 | 0.08 | 0.051 ^a | >1200 ^a |
| 5 ppm C | 2.0 | 1000 | 0.02 | 0.005 ^a | >4400 ^a |
| 50 ppm C | 2.6 | 1300 | 1.3 | 0.091 | 20000 |
| FA sorption^c | | | | | |
| 0.5 ppm C | 4.0 | 2000 | - | - | 2000 ^b |
| 5 ppm C | 3.4 | 1700 | - | - | 1800 ^b |
| 50 ppm C | 0.77 | 380 | - | - | 420 ^b |

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704 ^a Lower-limit, apparent K_{dT} values, since equilibrium was not reached within experimental time-frames.705 ^b Long-term K_{dT} nearly equivalent to early time equilibrium K_{d1} .706 ^c Kinetic and equilibrium values taken from pre-equilibration step and prior to Pu addition.

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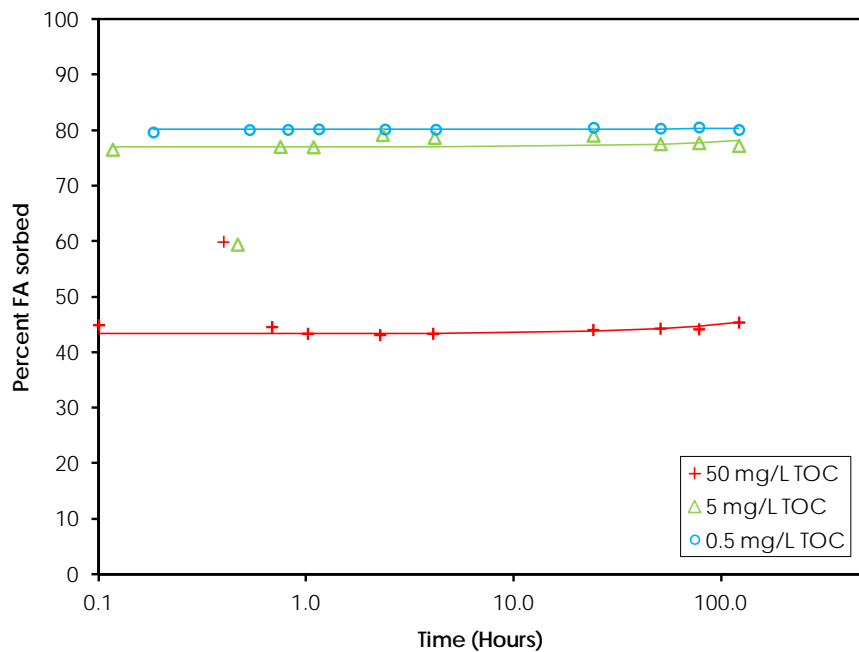
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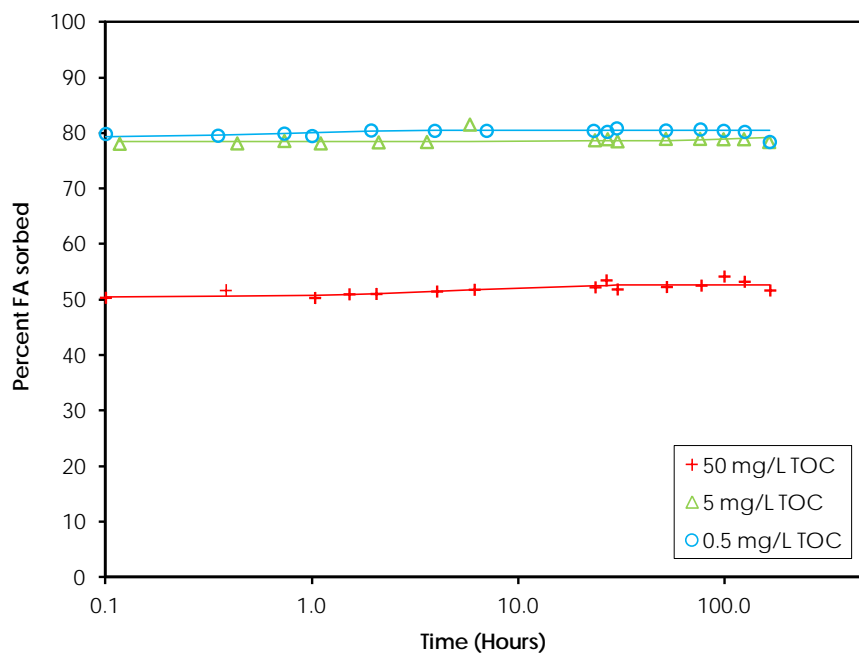
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FIGURES



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715 **Figure 1.** Kinetics of Suwannee River fulvic acid (FA) sorption onto 2 g L⁻¹ goethite (pH=4,
 716 I=0.01 M NaCl) in the absence (top) and presence (bottom) of 10⁻¹⁰ M Pu in *pre-coating* and *pre-*
 717 *complexation* experiments, respectively. Lines represent model fits to data as described in the
 718 Methods section.

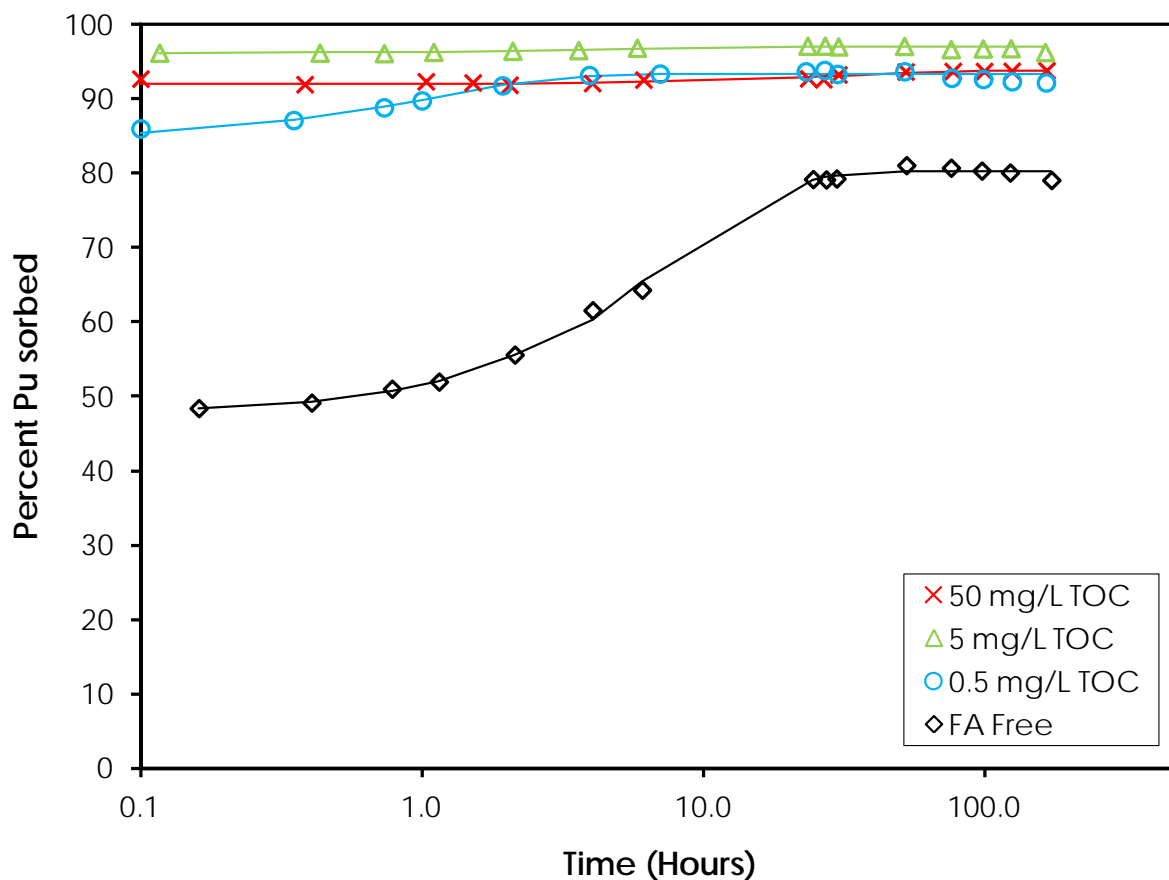


Figure 2. Kinetics of 10^{-10} M Pu sorption onto 2 g L^{-1} goethite ($\text{pH}=4$, $I=0.01 \text{ M NaCl}$) at various total, initial FA concentrations in solution (0 , 0.5 , 5 , and 50 mg L^{-1} TOC) in *pre-complexation* experiments. Lines represent model fits to data as described in the Methods section

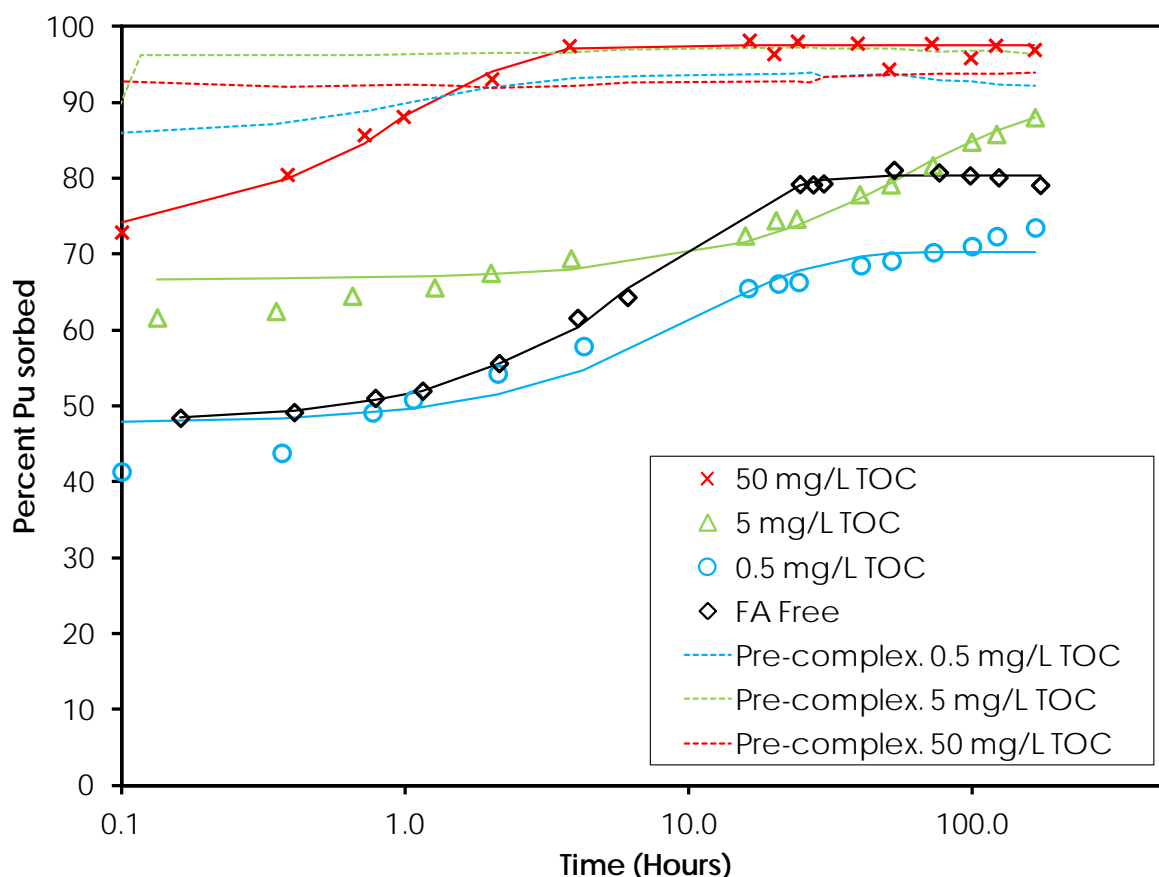


Figure 3. Kinetics of 10^{-10} M Pu sorption onto 2 g L^{-1} goethite ($\text{pH}=4$, $I = 0.01 \text{ M NaCl}$) at various total, initial FA concentrations (0, 0.5, 5 and 50 mg L^{-1} TOC) in *pre-coating* experiments. Initial FA concentrations lead to 0.19, 1.88 and $10.97 \text{ mg TOC g}_{\text{goethite}}^{-1}$ on the mineral surface and 0.01, 0.11 and 1.14 mg L^{-1} TOC in solution during the Pu sorption step. Full lines represent model fits to data as described in the Methods section. Dashed lines show Pu sorption in *pre-complexation* experiments for comparison.

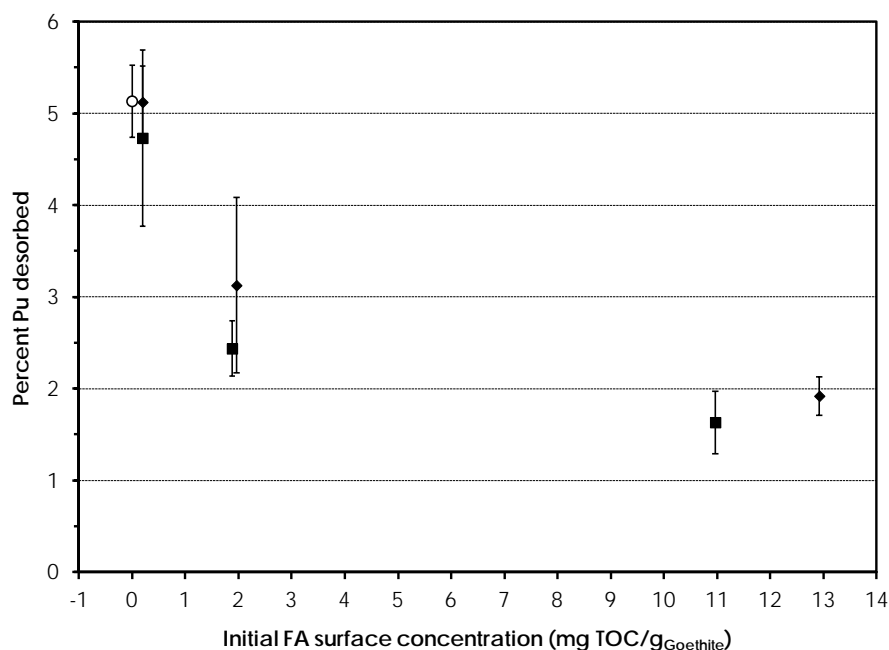
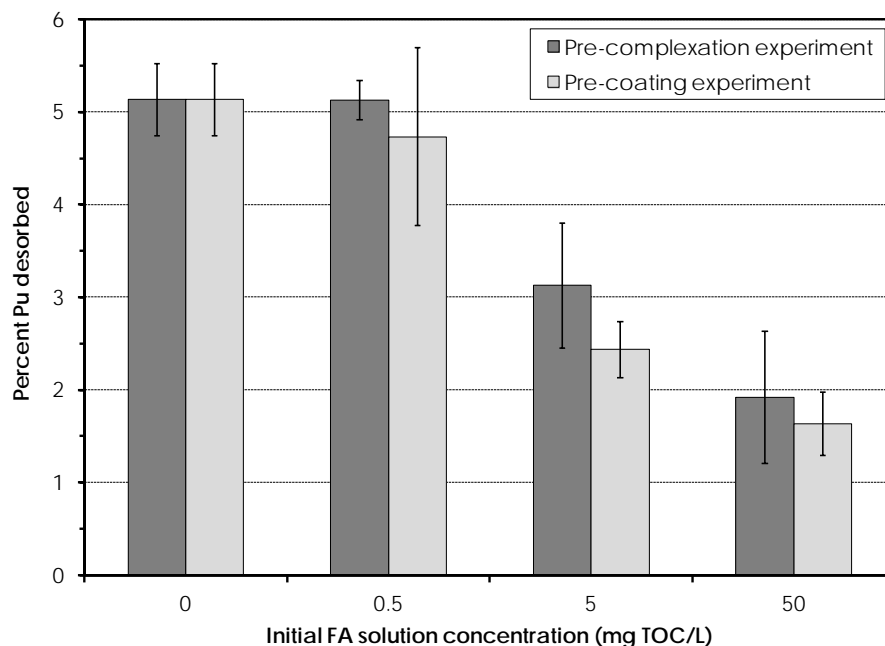


Figure 4. Fractions of Pu desorbed from goethite as a function of (a) FA solution concentrations at the beginning of sorption experiments (top), and (b) FA surface concentrations at the start of desorption steps (bottom). Zero FA concentrations represent binary Pu-goethite systems in triplicates. On bottom figure, Pu-goethite (○), *pre-complexation* (◆) and *pre-coating* (■) systems are distinguished by different symbols. All data are normalized for the same, exact desorption time-frame of 14.0 days based on a linear regression of the last four data points in each data set. Error bars represent propagated standard deviations from this linear regression (see text for details).